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Spatial and Temporal Variability in Emissions of Fluorinated Gases from a California Landfill

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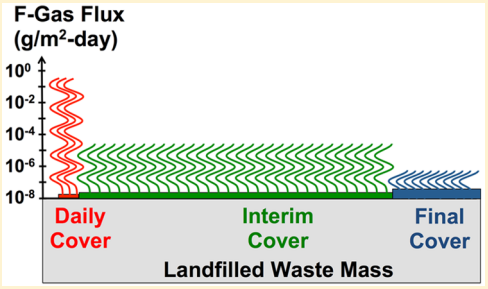
Supporting Information

ABSTRACT: Emissions of twelve (hydro)chlorofluorocarbons (F-gases) and methane were quantified using large-scale static chambers as a function of cover type (daily, intermediate, final) and seasonal variation (wet, dry) at a California landfill. The majority of the F-gas fluxes was positive and varied over 7 orders of magnitude across the cover types in a given season (wet: 10^{-8} to 10^{-1} g/m^2-day; dry: 10^{-9} to 10^{-2} g/m^2-day). The highest fluxes were from active filling areas with thin, coarse-grained daily covers, whereas the lowest fluxes were from the thick, fine-grained final cover. Historical F-gas replacement trends, waste age, and cover soil geotechnical properties affected flux with significantly lower F-gas fluxes than methane flux (10^{-4} to 10^{+1} g/m^2-day). Both flux and variability of flux decreased with the order: daily to intermediate to final covers; coarser to finer cover materials; low to high fines content cover soils; high to low degree of saturation cover soils; and thin to thick covers. Cover-specific F-gas fluxes were approximately one order of magnitude higher in the wet than dry season, due to combined effects of comparatively high saturations, high void ratios, and low temperatures. Emissions were primarily controlled by type and relative areal extent of cover materials and secondarily by season.



INTRODUCTION

Halogenated hydrocarbons including chlorinated and fluorinated species chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs), collectively termed (hydro)chlorofluorocarbons or F-gases, enter municipal solid waste (MSW) landfills through various waste stream pathways.[1] Historically, the two main uses of F-gases have been in insulation foams and refrigerants, with additional uses as aerosol propellants and cleaning agents. F-gases enter landfills in discarded appliances, construction and demolition wastes, and discarded heating/cooling units, transport refrigerated units, marine foams, fire suppressants, medical aerosols, and cleaning agents.[2,3] Most F-gases are potent greenhouse gases (GHGs) and CFCs and HCFCs also are ozone-depleting substances (ODSs).[1,4] Global warming potentials (GWPs, 100-year basis) vary from less than 1 to over 10 000 relative to CO_2 and atmospheric lifetimes vary from days to over 1000 years.[5]

The use of CFCs in refrigeration and insulation foams started in the 1920s and 1930s.[4] After the Montreal Protocol phased out CFCs by 1996, these gases were progressively replaced over time by HCFCs (lower atmospheric lifetimes compared to CFCs) and then HFCs (no significant ozone depletion compared to CFCs and HCFCs).[1] WMO[6] provided estimates of global emissions of CFCs, HCFCs, and HFCs to be 0.73, 0.76, and 0.69 $GtCO_2$-eq/year, with decreasing, relatively stable, and increasing trends, respectively over the previous decade. In California, emissions of CFCs, HCFCs, and HFCs were estimated to be 9.9, 10.3, and 18.9 $MtCO_2$-eq for 2014, with decreasing, relatively stable, and increasing trends in line with global trends, respectively over the previous decade.[7] California is the 15th largest emitter of GHGs globally, accounting for 2% of global emissions.[8] Comparing F-gas data for total global (2.18 $GtCO_2$-eq/year) and California-based (39.1 $MtCO_2$-eq/year) emissions[6,7] indicates that approximately 2% of global F-gas emissions are contributed by California similar to total GHG emissions trends.

Discrepancies between top-down and bottom-up estimates for ODS bank sizes and emissions as well as the need for representative emission rate data, have been identified for improving mitigation strategies.[9] In California, large discrepancies were reported between inventory-based F-gases emissions and field measurements.[7] Periodic ambient measurements are recommended for refining and calibrating inventory-based approaches to realistically evaluate both emission magnitudes at a given time and emission trends over time.[7]

While F-gases are trace components (ppmv or less) of LFG, emissions of F-gases are of concern due to their high GWP and potential for stratospheric ozone depletion.[5] Landfill releases of

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Table 1. MSW Landfill F-Gas Emissions from Static Flux Chamber Measurements[a]

gas	France Site I[11]	USA Site[12]	France Site II[13]	Northern Ireland Site[14f]
CFC-11	-7.92×10^{-5} to 7.63×10^{-5} (FC[b]); 2.08×10^{-5} (IC[c])	-1.84×10^{-4} to 7.53×10^{-6} (FC[d])	7.94×10^{-8} to 3.73×10^{-5} (FC[e])	$3.31 \times 10^{-5} \pm 2.65 \times 10^{-5}$ (SC[g]); $1.70 \times 10^{-5} \pm 3.30 \times 10^{-5}$ (SC[h])
CFC-12	-1.68×10^{-5} to 1.04×10^{-5} (FC[b]); 2.56×10^{-5} (IC[c])	-1.02×10^{-5} to 5.24×10^{-4} (FC[d])	-2.13×10^{-8} to 6.02×10^{-7} (FC[e])	$1.30 \times 10^{-5} \pm 1.38 \times 10^{-6}$ (SC[g]); $1.80 \times 10^{-5} \pm 4.65 \times 10^{-5}$ (SC[h])
CFC-113			-9.98×10^{-9} to 1.01×10^{-7} (FC[e])	$1.89 \times 10^{-5} \pm 6.72 \times 10^{-6}$ (SC[g]); $1.20 \times 10^{-5} \pm 1.56 \times 10^{-5}$ (SC[h])
CFC-114		3.82×10^{-6} to 2.53×10^{-4} (FC[d])		
HCFC-22	-4.89×10^{-6} to 2.26×10^{-5} (FC[b]); 5.74×10^{-5} (IC[c])		-6.10×10^{-8} to 9.07×10^{-6} (FC[e])	
HCFC-141b			3.63×10^{-6} to 6.66×10^{-5} (FC[e])	
HFC-134a			-2.59×10^{-6} to 5.49×10^{-6} (FC[e])	

[a]All flux values in units of (g/m^2-day), obtained using static chambers. [b]Final cover, loam, 0.8 m thick. [c]Intermediate cover, coarse sand, 0.4 m thick. [d]Final cover, clay, ~1 m thick. [e]Final cover, compacted clay or composite compacted clay/geomembrane, 1 m thick. [f]Data obtained in 2004, only positive flux reported. [g]Soil cover, type/materials not specified. [h]Likely soil cover, type/materials not specified.

Table 2. Cover Properties

property	daily cover			intermediate cover			final cover
material	auto fluff	green waste	soil	soil	soil	soil	soil
designation	AF	GW	ED	IC-1	IC-10	IC-15	FC
components	15 cm AF, 20 cm soil	13 cm GW, 13 cm soil	45 cm soil	80 cm soil	80 cm soil	82 cm soil	30 cm topsoil, 30 cm CCL[g], 60 cm base soil
landfill cell	12-north	12-north	12-north	1	10	15	1
operational status	active	active	active	inactive	inactive	inactive	closed
waste age (year)	0–16, 7.9 avg.	0–16, 9.5[e], 7.9[f] avg.	0–16, 7.9 avg.	17–29, 22.0 avg.	3–19, 13.6 avg.	3–9, 7.2 avg.	17–29, 22.0 avg.
cover fines content[a] (%)	NA[d]	NA	6.0	99.6	36.0	25.9	72.6
USCS[b] classification	NA	NA	GP-GC: poorly graded gravel with clay and sand	CH: fat clay	SC: clayey sand with gravel	SC: clayey sand with gravel	CH: fat clay with gravel
USDA[c] classification	NA	NA	loamy sand	clay	sandy loam	sandy loam	clay

[a]Fines content (i.e., particle size <75 μm). [b]Unified Soil Classification System. [c]United States Department of Agriculture. [d]Not applicable. [e]Wet season. [f]Dry season. [g]Compacted clay liner.

banked F-gases can constitute a significant portion of these gases entering the atmosphere with current use, stockpiling, and recycling constituting additional sources (e.g., 3, 7, 10). Conceptually, the landfill release pathways include (i) direct gaseous pathway releases during landfilling, diffusional releases through covers over time, and releases with recovered LFG from engineered collection systems; and (ii) indirect aqueous pathway releases through leachate collection, transport, and treatment systems. The fate of F-gases in the landfill environment and emissions are dependent on chemical and biological conversion processes (i.e., degradation and oxidation) in the waste mass and covers. Anaerobic degradation processes occur within the wastes and at depth in covers, whereas aerobic processes occur in covers at shallow depth. Additional chemical processes including sorption of the chemicals to the wastes and dissolution in the leachate also contribute to transport of F-gases within wastes and emissions from landfills (summarized in 3).

Existing literature quantifying gaseous F-gas emissions from landfills is sparse, with data for selected (hydro)-chlorofluorocarbons reported in a limited number of studies (Table 1). In general, previous data indicated that CFC and HCFC emissions were higher than HFC emissions; higher emissions were measured from thinner intermediate than thicker final covers; and emissions varied by up to 3 orders of magnitude for a given cover type at a given site, with the majority of data indicating 2 orders of magnitude or less variation at a given test location.

Regional site-specific data are needed to identify the extent of emissions and elucidate seasonal variability from a variety of landfill covers for input into GHG inventories and to inform future policy decisions on end-of-life management. In this project, using a direct static chamber method, we quantified spatial and temporal variations in emissions of banked F-gases from a California landfill for species no longer in widespread use (Montreal Protocol) and currently used replacement species. Of the 12 species investigated, HCFC-21, HCFC-142b, HCFC-151a, HFC-152a, and HFC-245fa emissions have not previously been quantified from landfills, nor have any F-gas emissions from daily covers been quantified. Also, detailed geotechnical engineering analyses of covers have not been conducted. We investigated surface fluxes of target F-gas species and methane as a function of cover characteristics, gas type, season, and waste age.

EXPERIMENTAL INVESTIGATION

Test Method. The static chamber method[15,16] was used to directly determine concentrations of target gases and thereby flux (positive or negative). The method allows for determination of flux from specific individual cover materials and types

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Table 3. Season-Specific Geotechnical Characteristics of Cover Materials

		wet season						dry season					
cover	G_s[a]	moist density (kg/m^c)	dry density (kg/m^c)	w^b (%)	S^c (%)	n^d	e^e	moist density (kg/m^c)	dry density (kg/m^c)	w^b (%)	S^c (%)	n^d	e^e
AF	1.48	585	509	15	12	0.66	1.91	505	447	13	8	0.70	2.31
GW	1.42	ND[f]	ND	129	ND	ND	ND	268	254	6	2	0.82	4.59
ED	2.66	1753	1603	9	38	0.40	0.66	2037	1879	8	54	0.29	0.42
IC-1	2.77	1168	956	22	32	0.65	1.90	1231	1176	5	10	0.58	1.35
IC-10	2.65	1335	1130	18	35	0.57	1.34	1230	1188	4	8	0.55	1.23
IC-15	2.62	1576	1326	19	51	0.49	0.98	1424	1400	2	5	0.47	0.87
FC	2.67	1273	1024	24	40	0.62	1.61	1122	1061	6	10	0.60	1.52

[a]Specific gravity. [b]Water content, gravimetric dry basis. [c]Degree of saturation. [d]Porosity. [e]Void ratio [f]Not determined.

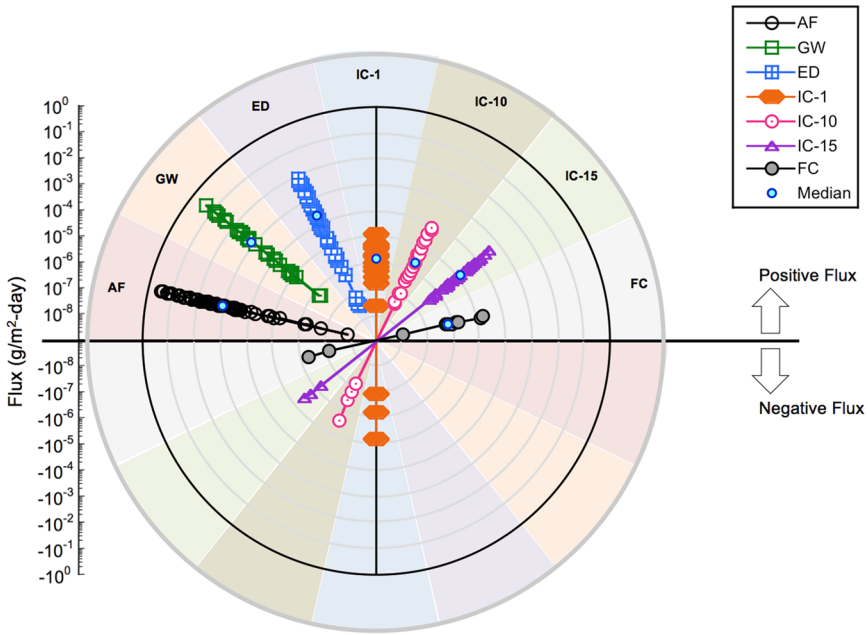

Figure 1. Variation of flux with cover type.

and has long been used for methane and trace gases at landfills to identify variability of surface flux across cover types and conditions (e.g., 11−13, 17−20). For this test program, custom-built, large-scale stainless-steel chambers with lateral dimensions of 1 × 1 m (1 m^2 measurement area) and 0.4-m height were used. A fan was used inside the chambers to circulate the gas collected to ensure uniform distribution prior to sampling. Gas samples were obtained using custom-built, 2-L capacity stainless steel evacuated canisters and analyzed by the Rowland−Blake Laboratory (University of California−Irvine) using two fully integrated VOC analytical systems. These systems consisted of three Agilent 6890 gas chromatographs, each housing two electron capture detectors, three flame ionization detectors, and a quadrupole mass spectrometer, which are unique in allowing quantification of concentrations in the parts per billion to parts per quadrillion range.[21] In the current study, the limit of detection varied between 1 and 60 pptv (F-gases) and 10−100 ppbv (methane) (additional details provided in Supporting Information).

Field Site. Tests were conducted at a large Subtitle D MSW landfill located in a temperate climate zone (Csa)[22] in northern California, USA. The average daily air temperature was 17.2°C and the annual precipitation was 596 mm at the site over the study period.[23] Meteorological data for the specific test dates and soil temperatures obtained during the tests are in Tables S1a and S1b, respectively. Municipal waste was the most significant constituent component of wastes by weight (82%), followed by construction and demolition waste (10%) and soil (4%) (additional details provided in Supporting Information and 3).

Field Test Program. The field test site had all three common cover types used at active MSW landfills: daily, intermediate, and final. Three materials were used for the daily covers, three materials were used for the intermediate covers, and one system was used for the final cover at the site. F-gas and methane fluxes were determined at seven locations representing all cover conditions: three daily, three intermediate, and one final (Table 2). The daily covers consisted of two alternative materials (auto fluff and green waste) and one traditional soil cover. The intermediate covers consisted of soils. The final cover system included a compacted clay liner and over- and underlying soil layers. The thickness of the covers, soil layer properties, and underlying waste ages varied among locations (Table 2). Geotechnical index and classification properties of the cover materials are provided in Table 3. At a given test location, quadruplicate flux tests were conducted using four chambers in a single testing event. The tests were repeated at the seven cover locations during the two main seasons in California: wet (February to April 2014) and dry (August 2014).

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Table 4. Surface Flux by Gas Type

	minimum (g/m^2-day)		maximum (g/m^2-day)	
gas type	wet	dry	wet	dry
CFC-11	2.27×10^{-6}	9.47×10^{-7}	2.57×10^{-1}	3.42×10^{-2}
CFC-12	-3.41×10^{-6}	1.63×10^{-6}	4.48×10^{-3}	1.12×10^{-3}
CFC-113	-5.22×10^{-7}	-5.96×10^{-7}	6.31×10^{-5}	9.05×10^{-6}
CFC-114	3.05×10^{-7}	1.06×10^{-7}	1.10×10^{-4}	3.23×10^{-5}
HCFC-21	1.47×10^{-6}	7.21×10^{-7}	2.63×10^{-1}	2.75×10^{-4}
HCFC-22	-1.60×10^{-6}	-2.30×10^{-6}	3.43×10^{-3}	1.46×10^{-3}
HCFC-141b	-5.59×10^{-6}	-5.01×10^{-7}	2.99×10^{-1}	7.58×10^{-3}
HCFC-142b	-3.50×10^{-7}	-7.04×10^{-8}	4.93×10^{-3}	9.68×10^{-4}
HCFC-151a	4.47×10^{-6}	4.74×10^{-5}	5.67×10^{-3}	9.40×10^{-4}
HFC-134a	5.69×10^{-7}	7.19×10^{-7}	3.79×10^{-2}	5.07×10^{-3}
HFC-152a	4.00×10^{-7}	1.70×10^{-6}	6.76×10^{-2}	1.27×10^{-3}
HFC-245fa	1.14×10^{-7}	9.74×10^{-9}	5.21×10^{-2}	8.77×10^{-3}

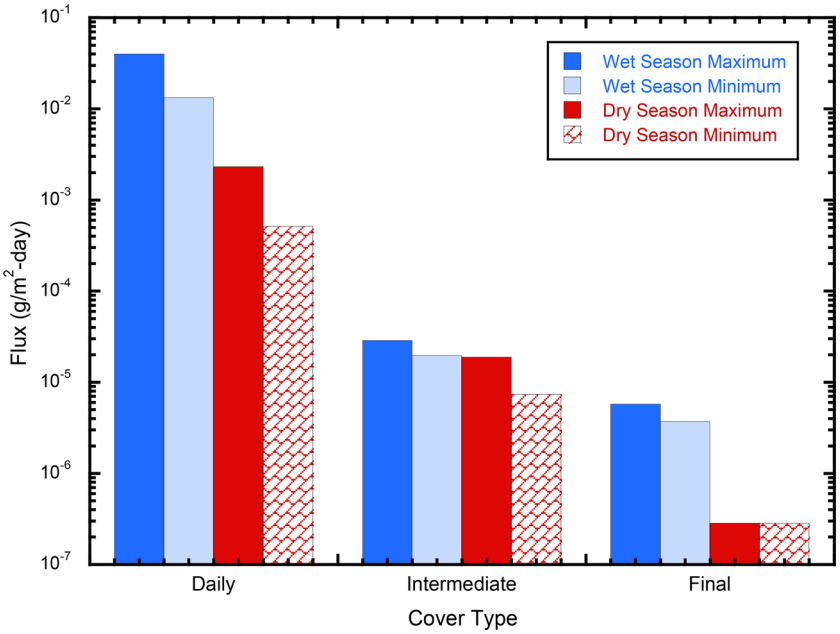

Figure 2. Seasonal variation of flux of F-gases.

The F-gases investigated were CFCs (CFC-11, CFC-12, CFC-113, CFC-114), HCFCs (HCFC-21, HCFC-22, HCFC-141b, HCFC-142b, HCFC-151a), and HFCs (HFC-134a, HFC-152a, HFC-245fa) for a total of twelve gases, representing historical replacement classes. General characteristics, main uses, and atmospheric properties of the F-gases are in Table S2.

RESULTS AND DISCUSSION

Surface Flux. Four types of surface flux data were obtained in the test program: positive flux, negative flux, data that did not meet the $R^2 \geq 0.9$ criterion (described in Supporting Information), and concentrations that were below the detection limit (BDL). Positive fluxes were determined at all seven test locations, whereas the occurrences of negative fluxes were low (3% of data) and limited solely to the intermediate and final covers. Data that did not fit the regression threshold were mainly from intermediate and final covers (61%) as opposed to from daily covers (39%) and most commonly occurred for the final cover. Similar to negative flux, BDL measurements were limited and only obtained from the intermediate and final covers, with no occurrences for daily covers.

Flux by Cover Type. Overall, F-gas flux varied from -10^{-6} to 10^{-1} g/m^2-day (Figure 1) with positive flux varying by 7 orders of magnitude in a given season: wet, 10^{-8} to 10^{-1} g/m^2-day; dry, 10^{-9} to 10^{-2} g/m^2-day (Table S3). F-gas flux decreased with the order daily to intermediate to final covers. The majority of the highest fluxes for individual F-gases were obtained from the alternative daily covers (83%) with more maximum fluxes from the auto fluff (65%) than the green waste cover (35%). The lowest fluxes were measured at the final cover (lowest median in Figure 1). The differences in flux between the daily and the intermediate covers (2−5 orders of magnitude) were higher than the flux differences between the intermediate and the final covers (1−2 orders of magnitude). In particular, the flux differences between the intermediate and final covers in Cell 1 were low, where the same high plasticity clay soil was used in both cover profiles.

Flux by Gas Type. The highest fluxes were measured for CFC-11, HCFC-21, and HCFC-141b (Table 4). Variation of maximum flux was higher within the CFCs (up to 4 orders of magnitude) than within the HCFCs (less than 2 orders of magnitude) and the HFCs (same order of magnitude). Negative fluxes were obtained for CFCs and HCFCs, with no

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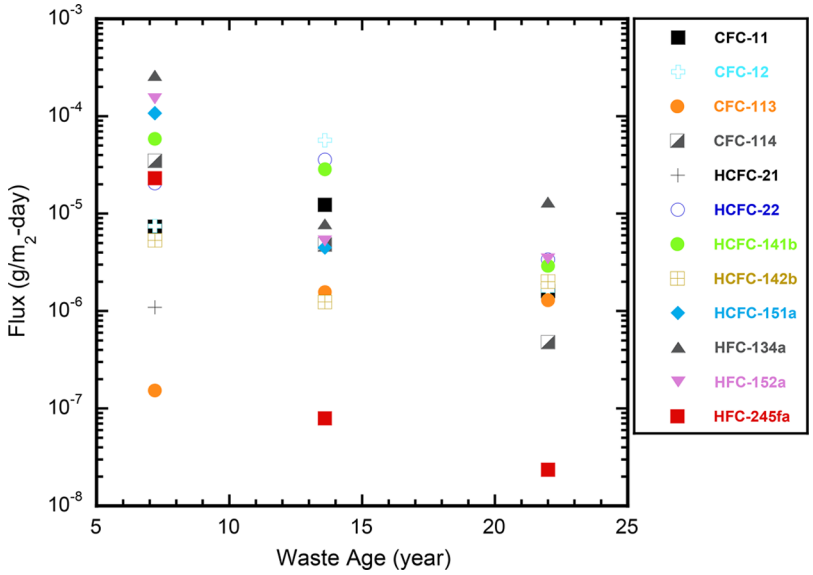

Figure 3. Variation of maximum flux with waste age.

negative flux measured for HFCs, the most recently used replacement species analyzed in the study.

The measured maximum F-gas fluxes (Table 4) are higher than the values reported in the literature (Table 1). These higher fluxes resulted from the daily covers, which were not included in previous studies. When only intermediate and final covers are considered (Table S3), the CFC fluxes are approximately 1 order of magnitude lower; HCFC fluxes are generally in line with up to 1 order of magnitude higher; and HFC fluxes are 1−2 orders of magnitude higher than the fluxes reported in the literature (Table 1). The data in the literature had been obtained in the 2000s. The current study, conducted approximately a decade later, captured the historic replacement trends for (hydro)chlorofluorocarbons in MSW and also was in line with the current global emission trends.

Flux by Season. Average maximum and minimum fluxes in each season are presented in Figure 2. The wet season fluxes were consistently higher than the dry season fluxes for all three cover types by approximately 1 order of magnitude. Lower methane emissions in the wet than dry season were reported for California based on field analysis and modeling,[24] in agreement with the observed seasonal F-gas emission trends in this study.

Flux by Waste Age. Variation of species-specific maximum flux with waste age is presented in Figure 3 for intermediate covers that were installed over variable-age wastes. Highest variation (over 3 orders of magnitude) was observed for the younger wastes. In general, flux and variation in flux decreased as the waste age increased. The most significant decrease for an individual gas (3 orders of magnitude) was determined for HCFC-245fa, the newest replacement F-gas. Fluxes of recent HCFCs and HFCs varied more with waste age than fluxes of the old F-gases (CFCs). Variations in flux with waste age were in line with the historical replacement trends for F-gases.

Flux Discussion. Inter- and intracover type and chemical species variations of F-gas flux were high, whereas seasonal variations were relatively low. Flux varied up to 7 orders of magnitude among the test locations and within a given test location (Table S3). For a given cover type, the flux varied by 5−7, 2−3, and 4 orders of magnitude for daily, intermediate, and final covers, respectively (Figure 1). For a given F-gas species, flux varied by 2−6, 3−6, and 5−7 orders of magnitude for CFCs, HCFCs, and HFCs, respectively (Table 4). For a given F-gas species at a given location, flux variation was relatively low and ranged from 0 to 4, 0 to 3, and 0 to 1 orders of magnitude for daily, intermediate, and final covers, respectively, with the great majority of the variations (91%) $\leq$ 2 orders of magnitude. The seasonal flux difference for a given cover location and chemical species was generally 1 order of magnitude. The greater variations in flux by location and chemical species than by season indicate that physical and chemical factors of cover characteristics, gas type, and waste age have greater influence on F-gas emissions than seasonal differences in climatic factors precipitation and temperature. The ranges of cover-specific F-gas fluxes reported herein can be used as guidelines for landfills with similar cover conditions.

The AF daily cover allowed high emissions. Combined with its low thickness, F-gases potentially present in the incoming AF[3] and outgassing of these at the landfill site likely contributed to the high emissions. A wide variety of materials including foams, spray-on-slurries, geosynthetics, and byproducts (e.g., sludges, ash, shredded tires, green waste, C&D waste, contaminated soils, auto fluff) are used as alternative daily covers (ADCs) due to various operational advantages over traditional soil daily covers.[25] Some of these materials potentially contain F-gases (or other trace gases). General requirements and specifications to assess the suitability of ADCs are included in standards[25−27] and regulations.[28] In ASTM specifications, analysis is included only for CFC-11 and CFC-12. No testing requirements for detecting chemical species are included in California regulations. Use of various wastes and byproducts as ADCs should be assessed to prevent environmental impacts due to the presence of trace chemicals. Also, transformation pathways within the ADCs need to be identified to assess effects on emissions. The GW daily cover also allowed high emissions. While the GW cover temperatures were consistently higher than ambient air temperatures and the temperatures of all other covers (Table S1) indicating potential for high biochemical activity (e.g., 18), transformation (i.e., oxidation/degradation) of the F-gases likely was limited due to the low thickness of the cover and low residence times of the gases. Potential transformation of F-gases in the higher-

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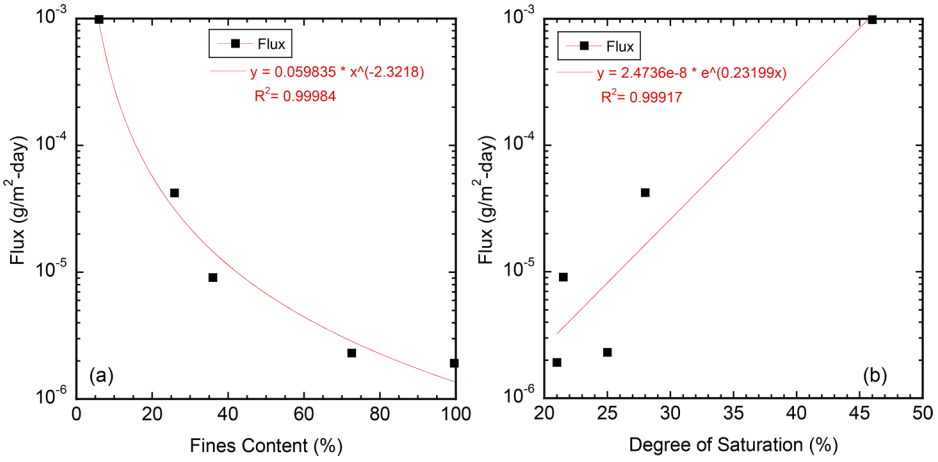

Figure 4. Variation of F-gas flux with fines content (a) and degree of saturation (b).

thickness ED soil daily cover resulted in the lower flux from this cover compared to the ADCs.

F-gas flux was influenced by the geotechnical properties of the covers. A strong inverse relationship was observed between the fines content (Table 2) and average flux for soil covers (Figure 4a). As the particle size decreases and soil type varies from coarse- to fine-grained, three distinct phenomena occur in soil structure: (i) number of pores and amount of pore spaces increase and the soil pores become more occluded than interconnected, (ii) tortuosity of flow paths increases, and (iii) more water is held (by strong electrochemical forces in addition to gravitational forces and surface tension) and residual state of saturation increases. All three phenomena result in increased resistance to fluid transfer.[29−31] Void ratio, porosity, and water content increase and density decreases with increasing fines content (Table 3), which also resulted in decreasing average flux from the soil covers (Figures S1a−S1d). Fines content (readily determined using disturbed samples without requiring intact samples) can be used as a preliminary selection tool for identifying cover materials with low gas flux potential.

The relative fraction of water in the soil pores also influenced flux. Average flux increased with increasing degree of saturation (Table 3) for the soil covers (Figure 4b). Decreasing retardation of gaseous transport of volatile organic chemicals with increasing water saturation and higher sorption capacity for dry than wet soils that reduces transport velocity were reported for unsaturated soils.[32] Oxidative methane consumption decreased with increasing degree of saturation for cover soils in laboratory experiments and numerical simulations (e.g., 33). These findings (reduced retardation/sorption/consumption) are in line with our field observations of increased flux with increasing saturation.

Seasonal flux variations also were influenced by cover geotechnical properties. For a given cover, water content and degree of saturation were higher in the wet than the dry season (Table 3). While water-filled pores in soils were reported to impede advective and diffusive gas flows for cases with no chemical or biological reactions within a system,[34] in the reactive cover environments[33] the combined effects of reduced sorption and decreased retardation allowed for easier transport of gases in the wet season. Increased effective stress due to development of negative porewater pressures during drying of the soils[35] resulted in lower void ratios (Table 3) and reduced fluxes in the dry season. Seasonal desiccation did not progress to formation of visible macro-cracks in the covers. In addition, both air and cover temperatures (Table S1) were consistently higher in the dry than the wet season, which likely promoted biological/biochemical transformation processes (e.g., 18) resulting in the lower fluxes. Determination of geotechnical properties is recommended for assisting in mechanistic explanation of observed flux behavior in different cover systems in the field. Also, in laboratory analysis of transformation and degradation processes of LFG constituents including F-gases, soils need to be analyzed at representative phase characteristics/soil macro and microstructure (which are not unique for a soil type) simulating field placement and service conditions.

F-gas concentrations in composite LFG from the entire landfill at the inlet to the flare are provided in Table S4a. Ambient F-gas concentrations obtained using the first (time zero) canisters from the chamber tests are in Table S4b. Based on data in Table S4, LFG concentrations of the individual F-gases were higher than the ambient concentrations (up to 4 orders of magnitude) with the exception of HCFC-21 (slightly higher ambient than LFG concentrations), which were in turn higher (up to 3 orders of magnitude) than background air concentrations.[36] The flux of HCFCs was higher than CFCs followed by HFCs. HCFCs represent historically intermediate F-gas species. The high HCFC fluxes likely resulted from large banks in the landfill including original incoming materials (not yet fully transformed within the waste mass or emitted from the facility) and gases contributed from potential dechlorination of CFCs.[37,38] In particular, HCFC-21 and HCFC-22 are significant products of transformation of CFC-11 and CFC-12, respectively in the waste mass.[37] The high ambient concentration of HCFC-21 also may have resulted from anaerobic degradation of CFC-11 in upper waste and lower cover layers at the test locations. In both wastes and cover soils, CFC-11 degraded faster than HCFC-141b under anaerobic conditions in laboratory batch tests[13,37] supporting higher accumulation of HCFCs in the waste mass and higher emissions through the covers. CFCs are the oldest chemicals studied and had the lowest average LFG and ambient concentrations, nevertheless the CFCs had higher flux than the HFCs likely due to still significant banks from continued disposal of the banned gases and relatively uniform distribution throughout the landfill with low variation with waste age and disposal cell (Figure 3). Even though HFCs, the newest chemicals included in the study, had the highest average concentrations in LFG and did not degrade in cover soils or within wastes in laboratory tests,[13,37] their flux was relatively

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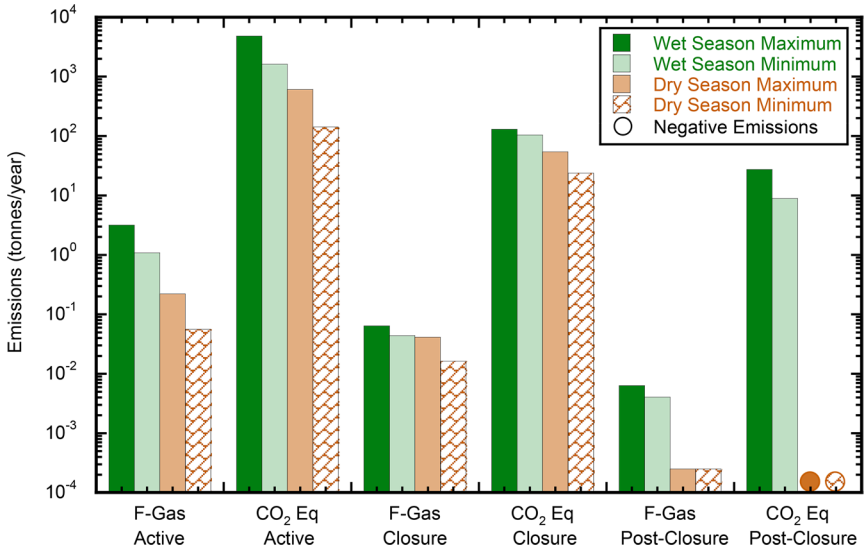

Figure 5. Landfill emissions of F-gases.

low. The HFCs were concentrated in newer wastes (Figure 3) with nonuniform distribution in the landfill resulting in sufficient accumulation only in some of the cells to produce appreciable flux. The composite gas from the entire landfill site did not reflect the spatial variability of flux or provide a representative indication of magnitude of flux for the F-gases.

Methane Flux. Measured absolute and positive ranges of methane flux were -10^{-2} to 10^{+1} and 10^{-4} to 10^{+1} g/m^2-day, respectively, with more negative fluxes measured for methane than the F-gases (Table S5a). Similar to F-gases, methane flux decreased with the order: daily to final covers; coarser to finer cover materials; and thin to thick covers. Differences between wet and dry season methane fluxes were on average 1 order of magnitude with no clear trend of a dominant season. Methane and F-gas flux trends were generally similar, however, the methane fluxes were orders of magnitude higher than the F-gas fluxes for a given cover type. Ratios of measured F-gas to methane emissions from the current study did not agree with estimated ratios provided in literature,[39] with differences up to 3 orders of magnitude (Table S5b). The methodology provided in the literature could not capture opposing emissions trends and no negative ratios were reported. Methane fluxes did not provide a surrogate for F-gas flux for the site investigated. The generation, transformation, and transfer processes in wastes and overlying cover materials that control the emissions of methane and F-gases are not fully comparable (e.g., 13, 37, 40); indicating that methane cannot provide a representative substitute for the emissions of F-gases. Process-based and field-validated models, similar to the CALMIM model developed and validated for field emissions of methane,[41] are required for predicting emissions of trace landfill gas components including F-gases.

Surface Emissions. Surface emissions from the landfill site (Figure 5) were estimated by scaling the measured fluxes to the entire landfill to (i) denote the range of emissions that may be expected with the current configuration of the different covers and (ii) assess emissions for changing configurations of the covers over time due to varying landfill operational conditions and landfill life stage. The scaling was conducted by using the relative areas of each cover type, which consisted of 3% daily, 84% intermediate, and 13% final cover, representing active landfilling conditions at the time of the field campaigns. The relative F-gas emissions (up to 3.19×10^0 tonnes/year) with respect to total (F-gas + methane) emissions (up to 2.69×10^3 tonnes/year) were generally small (Table S6a). The relative contributions of F-gas emissions were significantly higher for CO_2 equivalent analysis (up to 4.80×10^3 out of 8.01×10^4 tonnes/year) due to the amplified contributions of high global warming potential F-gases to environmental impact of landfill gas. For individual F-gases, the CO_2 equivalent CFC-11 emissions were higher than the emissions of the other gases (Table S6b) due to combined high flux and relatively high GWP (4660) of CFC-11.

All three cover types are used in active landfills, whereas intermediate and final covers are present at the time of closure of a site and only a final cover is present in the long term (i.e., postclosure). Emissions representing different lifetime stages beyond the active conditions were estimated with two scenarios: (i) using data only from intermediate and final covers; and (ii) using data only from final cover. The relative areas of the covers were redistributed accordingly over the waste placement footprint of the site. Emissions decreased from active to closure to postclosure conditions with higher reductions from active to closure than closure to postclosure conditions indicating the significant contribution of the daily covers to site emissions, even though these covers occupied a small surface area (3%) of the landfill (Figure 5). From active to closure conditions, estimated emissions decreased by 94−98% for wet and 71−91% for dry seasons. The type and relative areas of the different covers have significant influence on emissions. Emissions reflecting spatial variations and time-dependent evolution of cover conditions (type, thickness, relative area) need to be determined using measured data from different covers and adopted for use in representative greenhouse gas inventories. Periodic field assessment is required to establish temporal flux variations not only due to the biotic and abiotic transformations and biochemical degradation that the gases undergo in the landfill environment, but also due to the changes in formulation and use patterns of the incoming gases as well as variations in structure and geotechnical properties of covers.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b00845.

Analytical system, testing and site details, F-gas characteristics, LFG and ambient concentrations, F-gas and methane fluxes, total emissions, flux with phase relations (PDF)

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Notes

The authors declare no competing financial interest.

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